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METHOD AND APPARATUS FOR STERILIZING FOOD CONTAINERS

This application claims benefits of provisional application Serial No. 60/409,827 filed September 10, 2002.

FIELD OF THE INVENTION

The present invention relates to sterilization of food storage and transportation containers.

BACKGROUND OF THE INVENTION

Chlorine dioxide (ClO_2) is a strong oxidizing and antimicrobial agent. It has been reported to effectively inactivate bacteria, including pathogens, viruses, bacterial spores, and algae. In the food industry, chlorine dioxide has been used to sanitize food contact surfaces and food surfaces in the form of chlorine dioxide gas or a chlorine dioxide aqueous solution. For example aqueous chlorine dioxide solutions have been approved for use in washing fruits and vegetables in a manner that residual chlorine dioxide does not exceed 3 ppm. Gaseous chlorine dioxide is known as a disinfectant especially related to use in the medical sciences. For example, US Patents 4 504 442 and 4 681 739 describe use of gaseous chlorine dioxide to sterilize the gas-impermeable surfaces of implements commonly employed in practicing the medical sciences, such as those implements made of porcelain, ceramics, metal, plastics and glass. Treatment of the implements with 10 to 40 mg/L chlorine dioxide gas at room temperature and high relative humidity demonstrated sporicidal action. US Patent 6 235 240 describes apparatus and method for generating, administering, extracting and recovering sterilizing gas for sterilization and/or decontaminating microbial isolators.

Use of gaseous chlorine dioxide as a sterilizer in the food industry is limited. US Patent 6 277 328 discloses flooding a food storage transportation tank with gaseous chlorine dioxide for sterilization purposes, then pressurizing the tank with inert gas, and introduction of a bulk edible food product into the inert gas pressurized tank. Han et al. in "Efficacy of chlorine dioxide gas as a sanitizer for tanks used for aseptic juice storage", Food Microbiol, 16:53-61 (1999) describes surface

sterilization of aseptic juice storage tanks using gaseous chlorine dioxide gas.

Prevention of foods from spoilage or contamination with microorganisms, including spoilage bacteria, yeast, molds, and pathogenic bacteria, has been a large challenge for the food industry. Currently, steam or aqueous sanitizers are widely used to sanitize small size or bulk food storage or transportation tanks in the food industry. For instance, 25 ppm iodine solution is used to sterilize of bulk storage tanks of orange juice without rinse. To completely sanitize the surface of the entire tank, however, the tank must be filled up with the iodine solution. It takes a week or longer to sterilize a million-gallon tank. After sterilization, the huge volume of waste iodine solution must be stored or disposed of in appropriate manner.

SUMMARY OF THE INVENTION

The present invention provides method and apparatus for treating a container for food to sterilize or sanitize the container, which may be a fixed-site bulk storage container or transportable container including a tanker truck. The invention uses chlorine dioxide gas that is circulated through the container for a time, then removed from the container, and reclaimed such as preferably by dissolving in a solvent, such as, for example, water.

In illustrative embodiments of the invention, the chlorine dioxide gas is generated or produced outside or inside the container, is circulated for a time through the container via a conduit loop communicated to the container, then is flushed from the container, and is reclaimed by dissolving in water.

The invention is advantageous to sterilize food storage or transport containers for foods, such a orange juice, tomato puree, fruits, vegetables, grains, and fermented foods. The invention is further advantageous in that the chlorine dioxide gas is easily produced, circulated, and reclaimed, that the chlorine dioxide gas is effective to against organisms on any

gas-exposed surfaces of the food container, and that low residues of chorine dioxide are present on food or food-contact surfaces.

The above objects and advantages of the invention will become apparent from the following description of the invention.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic block diagram of a chlorine dioxide gas treatment apparatus pursuant to an embodiment of the invention.

Figure 2 is a schematic block diagram of a chlorine dioxide gas treatment apparatus pursuant to another embodiment of the invention.

Figure 3 is a schematic block diagram of a chlorine dioxide gas treatment apparatus pursuant to a still further embodiment of the invention.

DESCRIPTION OF THE INVENTION

The invention provides method and apparatus for sterilization or sanitation of an empty food tank or container 1 of Figures 1, 2 and 3. The container 1 can be a fixed-site storage container or a transportable container, such as, for example, a tanker truck. The invention can be practiced with food containers comprising closed vessels, containers, or tanks that demand a sterilized, sanitary or aseptic condition or reduced microbial concentration to store or transport foods. For instance, most fruit juices or beverages need to be aseptically stored or transported at refrigerated temperature before packing and marketing. Also for instance, the invention can be practiced to sterilize tanks or containers used for fermentation in any biotechnology industry, such as alcohol, beer, or pharmaceutical production.

A typical conventional tank or container 1 for food storage or food transportation will include a lower valve connection C1 and upper valve connection C2 to the container

Pursuant to the invention, chlorine dioxide gas is generated or produced outside or inside the empty container 1, is circulated through and inside the container for a time, then is removed from the container, and is reclaimed by dissolving in a solvent, such as for example water.

The chlorine dioxide gas can be produced outside the food container 1 using any type of conventional chlorine dioxide gas generator, such as a CDG gas generator available from CDG Technology, Inc. Bethlehem, PA. A chlorine dioxide gas generator 3 is shown in Figure 1 with connection with EXAMPLE 1 below.

Alternately, the chlorine dioxide gas can be produced outside or inside the container 1 by vaporization by bubbling a high concentration chlorine dioxide aqueous solution S (e.g. 1 to 20 g/L chlorine dioxide in water) with a suitable vaporizing gas, such as for example, air, nitrogen or other vaporizing gas. For example, the chlorine dioxide gas can be produced outside the container 1 by bubbling a chlorine dioxide aqueous solution residing in a chlorine dioxide gas generation tank 3' as shown in Figure 2 in connection with EXAMPLE 2 below.

The chlorine dioxide gas can be produced inside the container 1 by bubbling a high concentration chlorine dioxide aqueous solution S residing in the container 1 itself with a suitable vaporizing gas, such as air or nitrogen. This gas production technique is shown in Figure 3 in connection with EXAMPLE 3 below. The chlorine dioxide solution can be prepared by adding an amount of organic or inorganic acid to a sodium chlorite solution in a controlled manner, or it may be commercially purchased in a stabilized solution, such as an acidified chlorine dioxide solution or in a frozen state.

The concentration of chlorine dioxide gas in the carrier gas, the gas treatment time, relative humidity in the container 1, temperature of container 1, the types of target (resistant) microorganisms, container surface properties (coated or uncoated), and size of the target container are considered in practicing the invention. The chlorine dioxide concentration, gas treatment time, relative humidity in the container, and temperature are the most important factors in practicing the invention. Typical exemplary ranges for these factors include, but are not limited to, 1 to 50 mg/L chlorine dioxide gas and balance air or nitrogen, 10 minutes to 2 days exposure time, 30%

to 100% relative humidity, and 3-45 degrees C temperature. Preferred ranges for these factors include, but are not limited to, 10 to 15 mg/L chlorine dioxide gas and balance air or nitrogen, 30 minutes to 8 hours exposure time, above 80% relative humidity, and 3-25 degrees C temperature.

When the chlorine dioxide gas is generated or produced outside the container 1 as shown in Figures 1 and 2 in connection with EXAMPLES 1 and 2, the gas mixture (chlorine dioxide and air or nitrogen) is circulated inside and through the container via gas supply conduit 10 communicated to valve connection C1 at the bottom of the container 1 and via gas exhaust/circulation conduit 14 communicated to valve connection C2 at the top of the container 1. Conduit 14 is communicated to conduit 10 to thereby form a circulation loop L communicated to the container 1 for recirculating the gas mixture in and through the container 1 using fans or pumps 2 in conduits 10, 14 in Figures 1 and 2. Fans or pumps 2 proximate chlorine dioxide gas-dissolving tanks 5 are not energized at the time that the gas mixture is being circulated through container 1. The gas mixture including the chlorine dioxide gas is circulated in the container 1 for the selected gas treatment or exposure time.

When the chlorine dioxide gas is produced in-situ inside the container 1 as shown in Figure 3 in connection with EXAMPLE 3, the gas mixture is circulated therein via conduits 10 and 14 (forming a circulation loop L) using only pump 2' in conduit 14 for the selected gas treatment or exposure time. After the desired chlorine dioxide gas concentration is achieved in container 1, the chlorine dioxide solution is pumped from container 1 to a storage tank, and pump 2' in conduit 10 is de-energized.

After the selected exposure time of the container to the gas mixture, the gas mixture is removed or evacuated from container 1 by flushing the container with sterile (filtered) nitrogen, air or other suitable gas from source 15 (e.g. a compressed gas

cylinder) at a pressure in the range of 1000 to 6000 psi via the gas supply conduit 10 to remove the chlorine dioxide gas/air or nitrogen mixture from the container 1 via conduit 14 at the top of the container 1.

In Figure 1, a valve V is controlled to communicate the air or nitrogen source 15 with the gas supply conduit 10, rather than with the gas generator 3. In Figure 2, valve V is controlled to interrupt flow of gas from source 15 to the gas generation tank 3'.

During flushing of the container 1, fresh nitrogen gas or air from source 15 is fed into container 1 and the fans or pumps 2 proximate the chlorine dioxide gas-dissolving tanks 5 are energized to draw the chlorine dioxide gas/air or nitrogen mixture via conduit 16 through a suitable solvent, such as water, in tanks 5. The exhausted chlorine dioxide gas is dissolved in the solvent, such as for example water, in the chlorine dioxide gas-dissolving tank(s) 5. A recycled aqueous solution of chlorine dioxide is thus prepared in tank(s) 5 and can be stored there for future vaporization of the chlorine dioxide gas by bubbling as described in Example 2 and 3 in a next sterilization run or operation. Alternately or in addition, the chlorine dioxide solution in tank(s) 5 can be pumped by pump 8 out of the tanks 5 and used for sanitation of equipment, raw food materials, (such as fruits and vegetables), wall surfaces, and floor surfaces.

The gas exiting from tank(s) 5 can include some residual undissolved chlorine dioxide gas and can be neutralized by flowing it through one or more chlorine dioxide neutralizing columns 6, particularly over a reducing agent (not shown), such as soda lime (for nitrogen flushing) or sodium thiosulfate, packed in column(s). The reducing agent reduces residual chlorine dioxide gas to less than 0.1 ppm. The remnant air, nitrogen or other gas then exits the column(s) 6 to ambient air.

A monitoring system 7 is schematically illustrated for monitoring chlorine dioxide gas concentration, temperature, and pressure, as well as relative humidity in the container 1. For

purposes of illustration and not limitation, the concentration of gaseous and aqueous chlorine dioxide may be determined by any of the standard methods including, but not limited to, DPD-glycine colormetric method (EPA approved), chlorophenol red colormetric method, iodometric titration method, amperometric titration method (EPA approved), and direct absorbance method as described by Greenberg et al., "4500-C102C. Amperometeric method I. In Standard methods for the examination of water and wastewater" (18th edition), pp. 4-55 and 4-56, The American Public Health Association, Washington, D.C. (1992). The DPD-glycine titration method is especially useful to measure both gaseous and aqueous chlorine dioxide concentrations. For example, to measure chlorine dioxide concentration in air or nitrogen, a sample is prepared using a 25 ml gas-sampling syringe to obtain a 15 ml sample of chlorine dioxide gas/air or nitrogen mixture. The sample is immediately dissolved in 15 ml deionized and neutralized water. Before injecting the gas into the water, some water is repeatedly drawn in and out of the syringe to dissolve the gas completely. A DPD colormetric analysis kit from Chemetrics, Inc. Calverton, VA can be used. To measure the low amount (e.g. less than 1 ppm) of residual chlorine dioxide in foods, the amperometeric titration method can be used. In a commercial production scale sterilization operation, chlorine dioxide gas concentration can be monitored using an on-line chlorine dioxide gas analyzer, such as a continuous chlorine dioxide monitor from Interscan Corporation, Chatsworth, California or from Applied Analytics, Inc., Chestnut Hill, Massachusetts.

For quick reference purposes, in Figures 1, 2 and 3 illustrating embodiments of the invention, reference numerals designate components as follows: 1-food storage or transportation tank or container, 2-on-line fan or pump to convey chlorine dioxide/air or N_2 gas mixture, 3-chlorine dioxide gas generator, 3'-chlorine dioxide gas generation tank, 3''-dispenser of gas (e.g. air or N_2) for chlorine dioxide gas generation, 4-air filter, 5-chlorine dioxide gas dissolving tanks, 6-chlorine

dioxide gas neutralizing columns, 7-monitors for chlorine dioxide gas concentration, temperature, pressure, and relative humidity, 8-pump for chlorine dioxide solution, and 9-sterile water or chlorine dioxide solution spray head.

In the EXAMPLES which follow, the target microorganisms used to determine the effectiveness of chlorine dioxide gas treatment were some spoilage microorganisms (set forth in the EXAMPLES) which are commonly found in spoiled orange juices. These organisms have demonstrated resistance to sanitizing agents currently used (e.g. aqueous iodophors) and other environmental stress (e.g. low pH and high heat). Methods for preparation and enumeration of these bacteria and fungi were followed according to the "Compendium of Methods for the Microbiological Examination of Foods", Vanderzant and Splitttoesser, 1992. Microbiological media for preparation and enumeration of microorganisms were obtained from Difco Laboratories, Detroit, Michigan.

Isolates of the six spoilage microorganisms were provided by a commercial juice processor and maintained on slants at 7 degrees C on Lactobacillus MRS agar (MRS) for L. BUCHNERI, l. BREVIS, and L. TUMURITUM, on tryptic soy agar (TSA) for L. MESENTEROIDES, and on potato dextrose agar (PDA) for CANDIDA TROPICALIS and S. CERVASIEA.

The following EXAMPLES 1, 2 and 3 are offered to illustrate the invention is more detail without limiting the invention.

EXAMPLE 1

A 420 L stainless steel tank coated with epoxy was used to study the efficacy of ClO_2 gas as a potential sanitizing agent for commercial epoxy-lined orange juice storage tanks. The ClO_2 gas treatment model system was illustrated in FIG. 1, which includes a storage tank 1, four on-line fans or pumps 2, a chlorine dioxide gas generator 3, two air filters 4, two chlorine dioxide gas dissolving tanks 5, chlorine dioxide gas neutralizing columns 6, chlorine dioxide gas concentration, temperature, pressure, and relative humidity monitor system 7, and a corrosion-resistant pump for chlorine dioxide solution 8.

For aseptic bulk tank storage of juices, *L. buchneri* is a concern due to its resistance to some sanitizing agents and procedures. In this study, *L. buchneri* was selected as a test strain. A 24 hour culture of *L. buchneri* was grown in 10 ml Lactobacillus MRS broth for 18 hours at 37°C, serially diluted in 0.1% peptone followed by enumeration on MRS agar.

Stainless steel strips (2.5 x 7 cm), coated with an epoxy identical to that used in aseptic storage tanks, were obtained and then individually wrapped in aluminum foil and placed in an autoclave and heated at 121°C for 30 minutes. Individual sterile test strips were then aseptically handled using sterile forceps and surface inoculated. A 20 μL droplet, from the cocktail suspension, was used to inoculate the surface so that final inoculum level was 10^7cfu/strip (inoculated area 6-8 cm^2). The inoculated test strips were air-dried in the laminar flow hood for 10 minutes prior to treatment. Then the strips were hung at the different positions (top, middle and bottom) inside the tank.

A CDG High-Performance Chlorine Dioxide Gas (CDG Technology, Inc. New York) laboratory generator was used to produce ClO_2 gas. Nitrogen-balanced 4% chlorine gas was used to generate 8% ClO_2 gas in nitrogen with a density of approx. 227 mg/L. The generated ClO_2 gas was fed into the tank by a fan 2 through an air filter 4 at 103 SCF/H flow rate. Before introducing ClO_2 gas, a little steam was fed into the tank to achieve over 85% relative humidity. After introducing specified amount of ClO_2 gas (10-15 mg/L), the gas mixture was circulated inside the tank for 30 or 40 min at 17-27°C. The concentration of ClO_2 gas was measured at the beginning and the end of treatment using the above DPD colorimetric titration. After the treatment, the tank was evacuated by flushing with filtered air for 30 or 45 min. After the evacuation the residue of ClO_2 in the tank was collected by rinsing the tank with 20 L deionized water, and then measured using the DPD method. The exhausted ClO_2 gas was passed through the dissolving tank 5 and the gas neutralizing columns 6. The treatment conditions are summarized in TABLE 1.

Following the ClO_2 gas treatment, each strip was removed immediately and aseptically transferred into a sterilized bottle containing 300 mL of sterile MRS broth. The broth with treated strips was incubated at 37°C for 72 hours. Presence or absence of growth, as indicated by turbidity of the medium, was noted upon inspection of the samples following the incubation period. Those samples that were turbid were recorded as positive. Those samplers that were clear were recorded as negative. Additionally, three positive and negative controls were conducted in parallel for each experimental trial. Positive controls were performed for each of the test organisms. Positive controls consisted of a sampling strip inoculated with *L. buchneri* and placed directly into broth without exposure to ClO_2 treatment. Growth was observed as turbidity in the medium after incubation. A negative control consisted of an uninoculated sterile strip, without exposure to ClO_2 gas, placed into

broth. Absence of growth, as indicated by a clear microbiological medium, was observed after incubation. The results are shown in TABLE 1.

TABLE 1. Inactivation of *Lactobacillus Buchneri* by chlorine dioxide gas in a 420L storage vessel

Conditions and Results	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Inoculation level on each strip (cfu)	4×10^7	1.8×10^7	1.8×10^7	1.1×10^7
Treatment time (min)	40	30	30	30
Initial temperature (°C)	26.8	25.8	23.5	19.9
Final temperature (°C)	26.1	25.1	22.8	17.3
Initial relative humidity (%)	93	89.2	89.6	87.8
Final relative humidity (%)	91	87.6	86.8	86.3
Flow rate of ClO_2 gas (SCF/H)	103	103	103	103
Feeding time with ClO_2 gas (sec)	56	50	45	50
Initial ClO_2 concentration (mg/L)	15.33	13.55	11.99	16.7
Final ClO_2 concentration (mg/L)	12.66	12.23	10.72	16.09
Flushing time with air (min)	45	30	30	30
Residual ClO_2 after evacuation (mg)	12.46	32.25	7.12	59.30
Results of growth inspection:				
Positive control	+++[a]	+++	+++	+++
Control	---[b]	---	---	---
Three strips at the upper of tank	--	--	--	---
Three strips at the middle of tank	---	---	---	---
Two strips at the bottom of tank	--	--	--	--

Note: a. "+" represents positive growth in one broth bottle.
b. "-" represents negative growth in one broth bottle.

All results of the four experiments showed that a 10^7 cfu/strip level of *L. buchneri* could be completely inactivated by 10-16 mg/L ClO_2 gas treatment for 30 or 40 min at 17-27°C and under approx. 85% relative humidity.

Moreover, the largest amount of residual chlorine dioxide in the 420 L tank after flushing with filtrated air was 59.3 mg, which is 0.88% of total chlorine dioxide (6720 mg) in the tank during treatment. For 420 L orange juice, the predicted residual concentration of ClO_2 is 0.14 mg/L (ppm). Since 0.1 mg/L is the permitted residual amount of ClO_2 in drinking water, a longer flushing with filtered air, like for one hour or more, needs to be run or flushing with sterile water after the treatment is suggested.

EXAMPLE 2

Vaporized ClO_2 from its solution is used to replace the ClO_2 gas generator employed in Example 1. A commercial treatment system is shown in FIG. 2, in which 1-10 g/L ClO_2 solution was stored in the generation tank 3' and vaporized by bubbling with filtered air or nitrogen. Other procedures are the same as described in Example 1.

In a laboratory study, ClO_2 gas treatment was carried out in a 10 L Irvine Plexiglass cylinder with a stainless steel shelf, where inoculated strips were hung at different positions (top, middle and bottom) in the cylinder. A Thermo-Hygro recorder (Control Company, Friendswood, TX) was used to monitor relative humidity and temperature inside the treatment cylinder. 1.4 g/L and 3.9 g/L ClO_2 solutions could be prepared by flowing ClO_2 gas (160 mg/L in nitrogen) through 100 ml deionized water in a 125 ml gas-washing bottle (Chemglass Inc., Vineland, NJ) at a 0.5 SCF/H flow rate for 5 min and for 15 min, respectively. The 160mg/L ClO_2 gas was produced from a CDG laboratory generator (CDG Technology, Inc., New York, NY). Vaporized ClO_2 gas and air mixture inside the cylinder was circulated by a diaphragm vacuum pump (KNF Neuberger, Inc., Trenton, NJ) at a 1 L/min flow rate. Before injection of vaporized ClO_2 gas, approx. 90% relative humidity was achieved by flowing the air inside the cylinder through water in a gas-washing bottle. After vaporizing 1.4 g/L ClO_2 solution for 5 min and 20 min, 8 mg/L and 9.5 mg/L ClO_2 gas concentrations were achieved, respectively. The residual ClO_2 in the solution was 27 mg/L after 20 min vaporization, suggesting 80% ClO_2 was vaporized. It also indicated that 68% of the vaporized gas was in gas phase and 32% was reacted with organic materials or absorbed by the moisture inside the cylinder. At the 9.5 mg/L ClO_2 gas concentration, the inoculated strips were treated for 30 min at room temperature.

A cocktail of the six test organisms (*Lactobacillus buchneri, Lactobacillus brevis, Lactobacillus tumuritum, Leuconostoc mesenteroides, Candida tropicalis,* and *Saccharomyces cerevisiae*) were used to inoculate the strips. Each strain was grown individually in 10 ml Orange Serum Broth (OSB) for 24 hours at 37°C. A mixed culture was prepared by combining 2 ml of each individual culture in a sterile test tube prior to inoculation. The mixed culture was serially diluted with 0.1% peptone solution and pour-plated on TSA followed by 48 hr incubation at 37°C. 100 µL droplets, from the cocktail suspension, were spotted on the epoxy surfaces of sterilized strips so that final inoculum level was 4.5×10^7cfu/strip (inoculated area 6-8 cm^2). The inoculated test strips were air-dried in a biosafety hood for 2 hours prior to treatment.

After the ClO_2 gas treatment, each strip was aseptically transferred to 300 ml sterile tryptic soy broth with 1% sodium pyruvate. The operation of transferring strips was conducted in a biosafety hood. The broth bottles with treated strip were incubated at 37°C for 72 hours. Presence or absence of growth was noted upon inspection of the samples following the incubation period.

All the ClO_2-treated samples showed negative results, suggesting that the treatment with 9.5 mg/L vaporized ClO_2 for 30 min was effective to inactivate 7 log of target spoilage organisms on epoxy surface. Such a vaporized ClO_2 treatment system has a large advantage over the system described in Example 1. It does not need the ClO_2 gas generator that requires chlorine gas. In some food processors, a storage tank with high concentration of chlorine gas is not preferred due to its safety concern. The vaporization of ClO_2 on site from its solution may be a preferred option for those companies. The ClO_2 solution may

preferably be prepared by adding certain amount of organic or inorganic acid to sodium chlorite in a controlled way. It also may be purchased in a stabilized solution and activated on site.

EXAMPLE 3

A sterilization system with a direct vaporization of ClO_2 solution in the target tanks or containers is shown in FIG. 3. In this system, a high concentration of ClO_2 solution (1-20 g/L) is prepared or added in the target tank 1 either from the bottom or from the top. Introducing ClO_2 solution from the top through a spray head 9 can facilitate the vaporization of ClO_2 in the tank. The air inside the tank was circulated by a low pressure gas pump 2' and bubbled through a gas dispenser 3'' at the bottom of the tank to form an air/ClO_2 gas mixture. During the circulation of the gas mixture by pump 2', most ClO_2 in the solution is vaporized, and the equilibrium was finally achieved so that the amount of ClO_2 was approximately 10-50 g/L of the gas mixture. The temperature of the treatment is important because it affects the vaporization of ClO_2. The solubility of ClO_2 increases as the temperature decreases. The solubility of ClO_2 can be up to 8 g/L at 20 degrees C and 2.63 g/L at 40 degrees C under 74.9 mbar partial pressure. The concentration of vaporized ClO_2 in the tank can be determined and controlled based on the amount of ClO_2 in solution, the temperature, and the volume of the tank.

Once the required concentration of ClO_2 gas is achieved, the solution is pumped out of the tank and then the ClO_2 gas mixture was continuously circulated for required treatment time, which may be for example 30 minutes to one or more days depending on the size of the tank. Since a high concentration of ClO_2 solution is used in the tank, there may be a high residue of ClO_2 solution on the tank surface. In the end of the treatment, therefore, a water rinsing procedure may be used to remove the residues by spraying sterile water through a spray head 9 at the top of the tank. The spraying water can also dissolve most of the chlorine dioxide gas inside the tank. After water spray for 30 minutes or longer, the solution at the bottom of the tank is removed out by a pump. Then, the tank is flushed with filtrated nitrogen or air to remove the residual ClO_2 gas. The nitrogen or air mixture flowing out of the tank passes through ClO_2 gas dissolving tanks 5 and neutralizing columns 6 before it is released into the environment.

This system does not require any chlorine gas storage tank and chlorine dioxide solution storage tank. The stabilized and concentrated ClO_2 solution is commercially available. Therefore, this system provides a simple and easily controlled operation.

Although the invention has been described in detail above with respect to specific embodiments thereof, those skilled in the art will appreciate that changes, modifications and the like can be made thereto within the spirit and scope of the invention as set forth in the appended claims.